# Functionalization of Hafnocene Oxamidide Complexes Prepared From CO-Induced $N_2$ Cleavage

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*Supporting Information*

**Contents**

## I. Experimental Section

**General Considerations.** All air- and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.[1] Toluene, benzene, pentane and heptane were further dried by distillation from "titanocene".[2] Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Argon and hydrogen gas were purchased from Airgas Incorporated and passed through a column containing manganese oxide on vermiculite and 4 Å molecular sieves before admission to the high vacuum line. Carbon dioxide was also dried over 4 Å molecular sieves before admission to the high vacuum line.

$^{1}$H NMR spectra were recorded on a Varian Inova 400 Spectrometer operating at 399.860 MHz. All chemical shifts are reported relative to $SiMe_4$ using $^{1}$H (residual) chemical shifts of the solvent as a secondary standard. $^{2}$H, $^{13}$C, $^{29}$Si, and $^{15}$N NMR spectra were recorded on a Varian Inova 500 Spectrometer operating at 76.848, 125.716, 161.83, 99.320 and 50.663 MHz, respectively. $^{2}$H, $^{29}$Si, and $^{13}$C chemical shifts are reported relative to $SiMe_4$ using chemical shifts of the solvent as a secondary standard where applicable. $^{15}$N chemical shifts are reported relative liquid to $NH_3$ using an external standard. The C-C coupling constants for **1-$(CO_2)_2$** in the main text are reported as an average of $^{2}J_{C\text{-}C}$ and $^{3}J_{C\text{-}C}$; these AA'XX' spin systems appear as effective triplets by $^{13}$C NMR spectroscopy and this lack of detail in the spectra prevented accurate simulation.

Mass spectra were acquired using a JEOL GCMate II mass spectrometer operating at 500 (LRMS) resolving power (20% FWHM) in positive ion mode and an electron ionization (EI) potential of 70 eV. Samples were introduced via a GC inlet using an Agilent HP 6890N GC equipped with a 30 m (0.25 mm i.d.) HP-5ms capillary GC column. The carrier gas is helium with a flow rate of 1 mL/min. Samples were introduced into the GC using a split/splitless injector at 230 ºC with a split ratio of 50:1. Infrared spectroscopy was conducted on a Mattson RS-10500 Research Series FT-IR spectrometer calibrated with a polystyrene standard. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ.

**Computational Details.** All DFT calculations were performed with the ORCA program package.[3] The geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level[4,5,6] of DFT. Relativistic effects were accounted for by including the zeroth-order regular approximation (ZORA).[7,8,9,10] The def2-TZVP(-f) basis set in the scalar relativistic recontraction reported by Neese et al. (segmented all-electron relativistic basis sets, SARC) was applied.[11,12] For all elements up to bromine, the SARC basis sets are simply scalar relativistic recontractions of the basis sets developed by the Karlsruhe group,[13,14] while for heavier elements, the primitives and contraction patterns were designed in refs 11 and 12. The Coulomb fitting basis set of Weigend[15] was used in uncontracted form in all calculations. The RIJCOSX[16,17,18] approximation was used to accelerate the calculations.

**Spectroscopic characterization of $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(I)(Br)(N(CH_3)N(CH_2Ph)C_2O_2)$ (2-$(CH_3I)(PhCH_2Br)$).** In a drybox, a J. Young NMR tube was charged with 0.010 g (0.009 mmol) of **2-$(CH_3I)$** dissolved in about 0.5 mL of benzene-$d_6$. While in the box, 5.5 µL

(0.045 mmol) of benzyl bromide was added via syringe. The tube was capped, shaken and the progress of the reaction monitored by $^1$H NMR spectroscopy. Full conversion occurred after 16 h at 65 ºC. $^1$H NMR (benzene-$d_6$): $\delta$ = 1.67 (s, 6H, Cp$Me_4$H), 1.69 (s, 6H, Cp$Me_4$H), 1.71 (s, 6H, Cp$Me_4$H), 1.94 (s, 6H, Cp$Me_4$H), 2.07 (s, 6H, Cp$Me_4$H), 2.24 (s, 6H, Cp$Me_4$H), 2.31 (s, 6H, Cp$Me_4$H), 2.45 (s, 6H, Cp$Me_4$H), 2.51 (s, 3H, N$CH_3$), 3.89 (s, 3H, N$CH_2$Ph), 5.49 (s, 2H, CpMe$_4H$), 5.53 (s, 2H, CpMe$_4H$), 6.85-7.00 (m, 5H, NCH$_2Ph$). {$^1$H}$^{13}$C NMR (benzene-$d_6$): $\delta$ = 11.25 (Cp*Me*), 11.99 (Cp*Me*), 12.98 (Cp*Me*), 13.00 (Cp*Me*), 13.37 (Cp*Me*), 13.82 (Cp*Me*), 14.10 (Cp*Me*), 14.61 (Cp*Me*), 31.55 (N$CH_2$Ph), 33.70 (N$CH_3$), 109.28, 112.22, 114.59, 117.20, 118.21, 120.71, 122.09, 122.98, 123.99, 126.87, 126.89, 129.59, 140.05, 138.55 (*Cp,* NCH$_2Ph$), (N(CH$_3$)(*C*O) and (N(CH$_2$Ph)(*C*O)) not determined. IR (KBr): $\nu$ = 1603, 1621 cm$^{-1}$ (C=N).

**Spectroscopic characterization of [($\eta^5$-C$_5$Me$_4$H)$_2$Hf]$_2$(I)(Br)(N(CH$_3$)N(CH$_2$CH$_3$)C$_2$O$_2$) (2-(CH$_3$I)(CH$_3$CH$_2$Br))**. This compound was prepared in a similar manner to **2-(CH$_3$I)(PhCH$_2$Br)** using 0.010 g (0.009 mmol) of **2-(CH$_3$I)** and 0.045 mmol of ethyl bromide added via calibrated gas bulb on a vacuum line, and full conversion to **2-(CH$_3$I)(CH$_3$CH$_2$Br)** was observed after 48 h at 23 ºC. $^1$H NMR (benzene-$d_6$): $\delta$ = 1.58 (t, 3H, NCH$_2CH_3$), 1.67 (s, 6H, Cp$Me_4$H), 1.69 (s, 6H, Cp$Me_4$H), 1.71 (s, 6H, Cp$Me_4$H), 1.94 (s, 6H, Cp$Me_4$H), 2.07 (s, 6H, Cp$Me_4$H), 2.24 (s, 6H, Cp$Me_4$H), 2.32 (s, 6H, Cp$Me_4$H), 2.46 (s, 6H, Cp$Me_4$H), 2.49 (q, 2H, NC$H_2$CH$_3$), 2.51 (s, 3H, NC$H_3$), 2.93 (q, 2H, N$CH_2$CH$_3$), 5.49 (s, 2H, CpMe$_4H$), 5.53 (s, 2H, CpMe$_4H$). {$^1$H}$^{13}$C NMR (benzene-$d_6$): $\delta$ = 11.26 (NCH$_2CH_3$), 12.00 (Cp*Me*), 13.00 (Cp*Me*), 13.01 (Cp*Me*), 13.37 (Cp*Me*), 13.63 (Cp*Me*), 13.82 (Cp*Me*), 14.11 (Cp*Me*), 14.61 (Cp*Me*), 31.56 (NC$H_3$) 40.68 (N$CH_2$CH$_3$), 109.29, 112.23, 114.61, 117.21, 118.23, 120.71, 122.98, 123.99, 126.87 (*Cp*), 1 *Cp*,

$N(CH_2CH_3)(CO)$ and $(N(CH_3)CO)$ not determined. IR (KBr): $\nu$ = 1605 $cm^{-1}$, 1623 $cm^{-1}$(C=N).

**Spectroscopic characterization of $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(Br)_2(N_2(CH_2CH_3)_2C_2O_2)$ (2-$(CH_3CH_2Br)_2$)**. This molecule was prepared in a similar manner to **2-$(CH_3I)_2$** with 0.010 g (0.011 mmol) of **2** and 0.11 mmol of ethyl bromide added via calibrated gas bulb on a vacuum line. After 24 hours at 65 ºC complete conversion to **2-$(CH_3CH_2Br)_2$** was observed by NMR spectroscopy. $^1$H NMR (benzene-$d_6$): $\delta$ = 1.33 (t, 6H, $NCH_2CH_3$), 1.72 (s, 12H, Cp$Me_4$H), 2.03 (s, 12H, Cp$Me_4$H), 2.07 (s, 12H, Cp$Me_4$H), 2.11 (s, 12H, Cp$Me_4$H), 4.14 (q, 6H, $NCH_2CH_3$), 5.22 (s, 4H, $CpMe_4H$). $\{^1H\}^{13}$C NMR (benzene-$d_6$): $\delta$ = 11.48 ($NCH_2CH_3$), 12.87 (Cp*Me*), 13.76 (Cp*Me*), 14.39 (Cp*Me*), 14.78 (Cp*Me*), 58.64 ($NCH_2CH_3$), 113.34, 114.75, 120.75, 122.70, 125.95 (*Cp*), 169.25 ($N_2(CH_2CH_3)_2C_2O_2$). IR (KBr): $\nu$ = 1586, 1621 $cm^{-1}$ (C=N).

**Spectroscopic characterization of $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(Br)(N(CH_2Ph)NC_2O_2)$ (2-$PhCH_2Br$)**. This compound was prepared in a similar manner to **2-$(CH_3I)$** using 0.010 g (0.011 mmol) of **2** and 6.5 μL (0.055 mmol) of benzyl bromide and required 1 h for complete conversion to **2-$(PhCH_2Br)$**. $^1$H NMR (benzene-$d_6$): $\delta$ = 1.60 (s, 3H, Cp$Me_4$H), 1.67 (s, 3H, Cp$Me_4$H), 1.70 (s, 3H, Cp$Me_4$H), 1.71 (s, 3H, Cp$Me_4$H), 1.79 (s, 3H, Cp$Me_4$H), 1.83 (s, 3H, Cp$Me_4$H), 1.96 (s, 3H, Cp$Me_4$H), 1.97 (s, 3H, Cp$Me_4$H), 2.06 (s, 3H, Cp$Me_4$H), 2.07 (s, 3H, Cp$Me_4$H), 2.09 (s, 3H, Cp$Me_4$H), 2.25 (s, 3H, Cp$Me_4$H), 2.29 (s, 3H, Cp$Me_4$H), 2.31 (s, 3H, Cp$Me_4$H), 2.33 (s, 3H, Cp$Me_4$H), 2.49 (s, 3H, Cp$Me_4$H), 4.39 (s, 1H, $NCH_2Ph$), 4.92 (s, 1H, $NCH_2Ph$), 5.25 (s, 1H, $CpMe_4H$), 5.55 (s, 1H, $CpMe_4H$), 5.59 (s, 2H, $CpMe_4H$), 7.07-7.29, 7.56 (m, 5H, $NCH_2Ph$). $\{^1H\}^{13}$C NMR

(benzene-$d_6$): δ = 11.25 (Cp*Me*), 11.99 (Cp*Me*), 12.98 (Cp*Me*), 13.00 (Cp*Me*), 13.37 (Cp*Me*), 13.82 (Cp*Me*), 14.10 (Cp*Me*), 14.61 (Cp*Me*), 31.55 (N*CH*$_2$Ph), 33.70 (N*CH*$_3$), 109.28, 112.22, 114.59, 117.20, 118.21, 120.71, 122.09, 122.98, 123.99, 126.87, 126.89, 129.59, 140.05, 138.55 (*Cp,* NCH$_2$*Ph*), (N(CH$_2$Ph)(*C*O)) and (N*C*O) not observed. IR (KBr): ν = 1624, 1653 cm$^{-1}$ (C=N).

**Preparation of [(η$^5$-C$_5$Me$_4$H)$_2$Hf]$_2$(H)$_2$((NSiH$^n$Hex)$_2$C$_2$O$_2$) (2-($^n$HexSiH$_3$)$_2$).** A J. Young NMR tube was charged with 0.010 g (0.011 mmol) of **2** approximately 0.5 mL benzene-$d_6$. A slight excess of *n*-hexylsilane (2.2 equivalents, 0.024 mmol) was added via calibrated gas bulb on a vacuum line and the resulting reaction mixture was shaken resulting in complete conversion to **2-($^n$HexSiH$_3$)$_2$** as judged by $^1$H NMR spectroscopy. $^1$H NMR (benzene-$d_6$): δ = 0.92 (t, 6H, NSiH$_2$(CH$_2$)$_5$C*H*$_3$), 1.34 (m, 4H, NSiH$_2$(C*H*$_2$)$_5$CH$_3$), 1.52 (m, 4H, NSiH$_2$(C*H*$_2$)$_5$CH$_3$), 1.60 (m, 4H, NSiH$_2$(C*H*$_2$)$_5$CH$_3$), 1.72 (s, 12H, Cp*Me*$_4$H), 2.00 (m, 4H, NSiH$_2$(C*H*$_2$)$_5$CH$_3$), 2.06 (s, 12H, Cp*Me*$_4$H), 2.19 (s, 12H, Cp*Me*$_4$H), 2.20 (s, 12H, Cp*Me*$_4$H), 4.96 (s, 4H, CpMe$_4$*H*), 5.22 (t, 4H, NSi*H*$_2$(CH$_2$)$_5$CH$_3$), 9.95 (s, 2H, Hf*H*). {$^1$H} $^{13}$C NMR (benzene-$d_6$): δ = 12.42, 12.78, 13.95, 14.77, 15.28 (SiH$_2$(CH$_2$)$_5$*C*H$_3$, Cp*Me*), 23.37, 25.03, 32.49, 33.44 (SiH$_2$(*C*H$_2$)$_5$CH$_3$), 107.37, 111.92, 115.13, 118.47, 119.80 (*Cp*), 175.32 (N$_2$(SiH$_2$(CH$_2$)$_5$CH$_3$)$_2$*C*$_2$O$_2$). IR (KBr): ν = 1560 cm$^{-1}$ (C=N), 2188 cm$^{-1}$ (SiH).

**Preparation of [(η$^5$-C$_5$Me$_4$H)$_2$Hf]$_2$(H)$_2$((NSiHPh$_2$)$_2$C$_2$O$_2$) (2-(Ph$_2$SiH$_2$)$_2$).** This molecule was prepared in a similar manner to **2-($^n$HexSiH$_3$)$_2$** with 0.010 g (0.011 mmol) of **2** and 4.4 µL (0.024 mmol) of Ph$_2$SiH$_2$. Immediate conversion to **2-(Ph$_2$SiH$_2$)$_2$** was observed. $^1$H NMR (benzene-$d_6$): δ = 1.72 (s, 12H, Cp*Me*$_4$H), 1.78 (s, 12H, Cp*Me*$_4$H), 1.86 (s, 12H, Cp*Me*$_4$H), 2.11 (s, 12H, Cp*Me*$_4$H), 4.78 (s, 4H, CpMe$_4$*H*), 6.47 (s, 2H, NSi*H*Ph$_2$), 7.06-

7.34 (m, 12H, NSiH*Ph*$_2$), 8.15 (m, 8H, NSiH*Ph*$_2$), 9.80 (s, 2H, Hf*H*). $\{^1H\}^{13}C$ NMR (benzene-$d_6$): $\delta$ = 13.35 (Cp*Me*), 13.40 (Cp*Me*), 14.62 (Cp*Me*), 15.29 (Cp*Me*), 108.14, 110.15, 116.55, 116.60, 121.95 (*Cp*), 130.47, 136.39, 137.92, 139.01 (SiH*Ph*$_2$) 176.15 ($N_2(SiHPh_2)_2C_2O_2$). IR (KBr): $\nu$ = 1567 cm$^{-1}$ (C=N), 2194 cm$^{-1}$ (SiH).

**Preparation of [($\eta^5$-$C_5Me_4H)_2Hf)_2(H)(I)((NSiH_2Ph)(NCH_3)C_2O_2)$ (2-($CH_3I$)($PhSiH_3$)).** In a drybox, a J. Young NMR tube was charged with 0.010 g (0.009 mmol) of **2-($CH_3I$)** and approximately 0.5 mL of benzene-$d_6$ was added. Approximately 1.2 equivalents of $PhSiH_3$ (1.3 μL, 0.011 mmol) was added via syringe and the tube shaken thoroughly. Monitoring the reaction by $^1H$ NMR spectroscopy established complete conversion to **2-($CH_3I$)($PhSiH_3$)**. $^1H$ NMR (benzene-$d_6$): $\delta$ = 1.56 (s, 6H, Cp*Me*$_4$H), 1.74 (s, 6H, Cp*Me*$_4$H), 1.80 (s, 6H, Cp*Me*$_4$H), 1.97 (s, 6H, Cp*Me*$_4$H), 1.99 (s, 6H, Cp*Me*$_4$H), 2.10 (s, 6H, Cp*Me*$_4$H), 2.16 (s, 6H, Cp*Me*$_4$H), 2.23 (s, 6H, Cp*Me*$_4$H), 3.67 (s, 3H, N*CH*$_3$, $^3J_{CH}$ = 4.4 Hz), 4.89 (s, 2H, NSi*H*$_2$Ph), 5.41 (s, 2H, CpMe$_4$*H*), 5.86 (s, 2H, CpMe$_4$*H*), 7.20-7.40 (m, 3H, NSiH$_2$*Ph*), 8.10 (m, 2H, NSiH$_2$*Ph*), 9.38 (s, 1H, Hf*H*). $\{^1H\}^{13}C$ NMR (benzene-$d_6$): $\delta$ = 11.99 (Cp*Me*), 12.01 (Cp*Me*), 13.45 (Cp*Me*), 13.56 (Cp*Me*), 14.96 (Cp*Me*), 15.07 (Cp*Me*), 15.20 (Cp*Me*), 16.13 (Cp*Me*), 46.49 (N*CH*$_3$), 107.34, 111.83, 113.43, 115.36, 115.41, 118.24, 120.29, 121.90, 122.34, 127.23 (*Cp*), 130.65, 136.64, 137.04, 138.07 (NSiH$_2$*Ph*), 170.33, 173.05 ((N(CH$_3$)(*C*O), (N(CH$_2$Ph)(*C*O), $^1J_{CC}$ = 72.5 Hz), 1 Cp not found. IR (KBr): $\nu$ = 1558 cm$^{-1}$ (C=N), 2119 cm$^{-1}$ (SiH).

**Representative oxamidate protonolysis of 2-($CH_3I$)$_2$.** Treatment of the hafnium oxamidide compound **2-($CH_3I$)$_2$** (0.075 g, 0.062 mmol) with 10 equivalents of HCl (as a dioxane solution) admitted via calibrated gas bulb resulted in liberation of

dimethyloxamide in high yield (>95% by $^1$H NMR spectroscopy), along with formation of 2 equivalents of **2-Cl$_2$**. The product mixture was washed several times with diethyl ether, affording 0.005 g (71%) of pure *N*, *N'*-dimethyloxamide as a white solid, confirmed spectroscopically by comparison to an independently prepared sample (*vide infra*). Similar results were achieved performing the protonolysis with ethanol (10 equiv added via syringe) instead of HCl.

**Spectroscopic characterization of *N*-alkyl and *N, N'*-dialkyloxamides.** The identities of *N*-methyl-*N'*-benzyloxamide,[19] *N*, *N'*-diethyloxamide,[20] and methyloxamide[21] were confirmed by comparison to their previously reported spectroscopic parameters.

**Independent synthesis of *N, N'*-dimethyloxamide.**[22] A 500 mL 3-neck round bottom flask fitted with an addition funnel was charged with 200 mL of THF, added via cannula on a Schlenk line. The flask was cooled to -78 ºC, the headspace was evacuated, and triethylamine (~0.01 mol) was admitted via vacuum transfer, followed by excess methylamine (~0.12 mol). The flask was warmed to 0 ºC and, with stirring, oxalyl chloride (5.2 mL, 0.05 mol) was added dropwise through an addition funnel, causing vigorous generation of HCl. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. After this time the solvent volume was reduced and the insoluble white material was filtered and recrystallized from ethanol, furnishing ~5 g (85%) pure *N*, *N'*-dimethyloxamide. $^1$H NMR (dimethylsulfoxide-$d_6$): $\delta = 2.66$ (d, 6H, C$H_3$) ($^2J_{HH}$=4.9 Hz), 8.67 (br s, 2H, N$H$). $\{^1H\}^{13}C$ NMR (dimethylsulfoxide-$d_6$): $\delta = 25.79$ ($C$H$_3$), 160.47 (N$_2C_2O_2$).

**Spectroscopic characterization of ethyloxamide.** $^{1}$H NMR (dimethylsulfoxide-$d_6$): $\delta$ = 1.03 (t, 3H, C$H_3$CH$_2$N) ($^{3}J_{HH}$=7.2 Hz), 3.13 (m, 2H, CH$_3$C$H_2$N), 7.74 (br s, 1H, N$H_2$), 8.02 (br s, 1H, N$H_2$), 8.70 (br s, 1H, CH$_3$CH$_2$N$H$). {$^{1}$H}$^{13}$C NMR (dimethylsulfoxide-$d_6$): $\delta$ = 14.41 ($C$H$_3$CH$_2$N), 33.66 (CH$_3$$C$H$_2$N), 159.99, 162.29 (N$_2$$C_2$O$_2$).

**Spectroscopic characterization of benzyloxamide.** $^{1}$H NMR (dimethylsulfoxide-$d_6$): $\delta$ = 4.31 (d, 2H, PhC$H_2$N), 7.2-7.4 (m, 5H, $Ph$CH$_2$N), 7.81 (br s, 1H, N$H_2$), 8.08 (br s, 1H, N$H_2$), 9.24 (br s, 1H, PhCH$_2$N$H$). {$^{1}$H}$^{13}$C NMR (dimethylsulfoxide-$d_6$): $\delta$ = 42.33 (Ph$C$H$_2$N), 118.14, 120.29, 120.35 ($Ph$CH$_2$N), 160.10, 162.16 (N$_2$$C_2$O$_2$).

**Independent preparation of 1-(I)(NCO).** A thick walled glass vessel was charged with 0.257 g (0.38 mmol) of **1-I$_2$** and approximately 10 mL of tetrahydrofuran. A slurry of 0.063 g (0.42 mmol) silver cyanate in approximately 5 mL of tetrahydrofuran was added dropwise to the reaction vessel with stirring. The vessel was degassed and then placed in an 80 ºC oil bath for three days. After this time, the volatiles were removed in vacuo and the desired product extracted into diethyl ether. The diethyl ether solution containing the product was concentrated to approximately 2 mL and then stored at -35 ºC. This procedure furnished 0.142 g (81 %) of pale yellow crystals identified as **1-(I)(NCO)**.

## II. Representative NMR Spectra

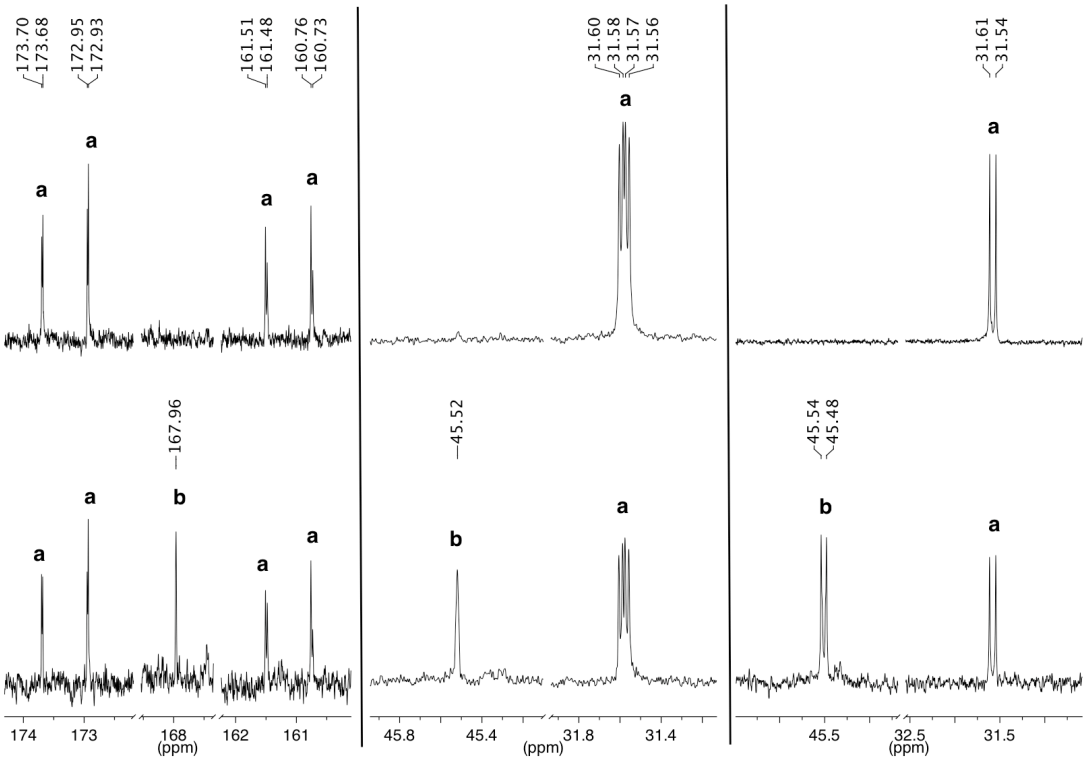



**Figure S1.** $N_2C_2O_2$ region (left) and N-$CH_3$ region (right) of the benzene-$d_6$ $^{13}C$ NMR spectrum of the reaction of **2** ($^{13}C$ labeled) with excess $^{13}CH_3I$ in benzene-$d_6$ after 5 minutes (top spectra) and after 8 hours (bottom spectra); Peaks labeled "**a**" correspond to **2-($^{13}CH_3I$)** and peaks labeled "**b**" correspond to **2-($^{13}CH_3I)_2$**.

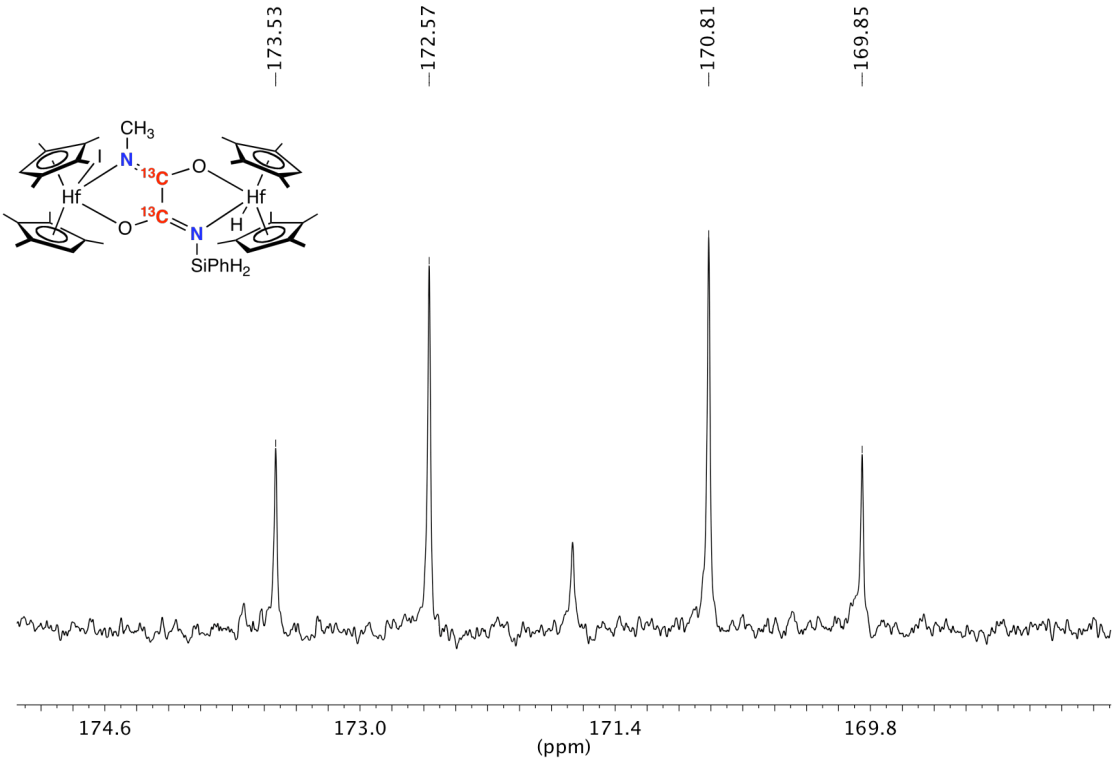



**Figure S2.** $N_2C_2O_2$ region of the benzene-$d_6$ $^{13}C$ NMR spectrum of the reaction of **2-($CH_3I$)** ($^{13}C$ labeled) with excess $PhSiH_3$ in benzene-$d_6$ after 5 minutes. Small center resonance attributed to impurity.

**III. Additional Representations of Solid State Crystal Structures.**

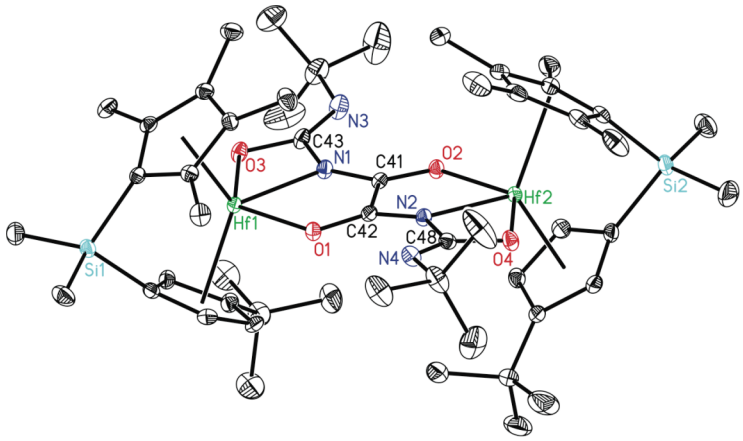



**Figure S3.** Representation of the solid state structure of (***R***, ***R***)-**1-(**$^{t}$**BuNCO)$_2$** at 30 % probability ellipsoids. Hydrogen atoms omitted for clarity.

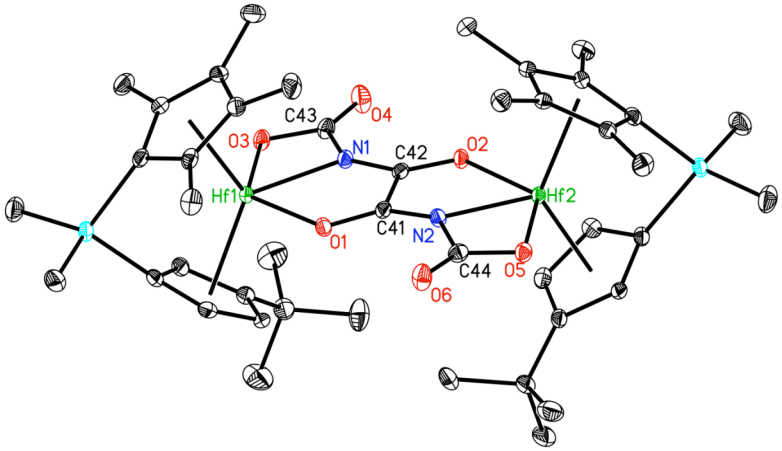



**Figure S4.** Representation of the solid state structure of (***R***, ***R***)-**1-(CO)$_2$** at 30 % probability ellipsoids. Hydrogen atoms omitted for clarity.

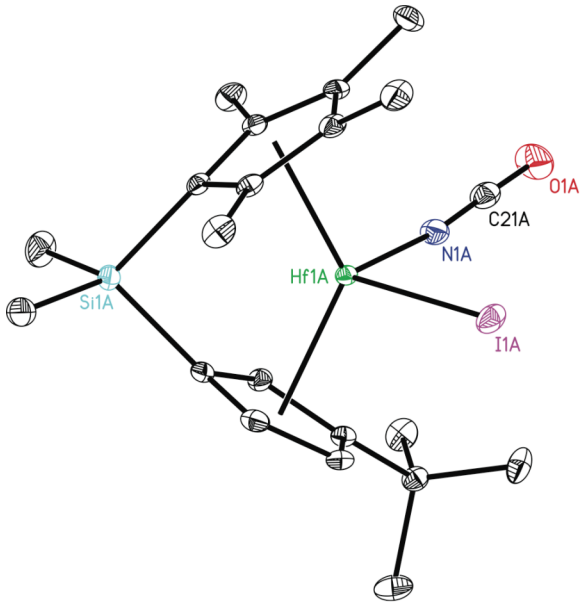
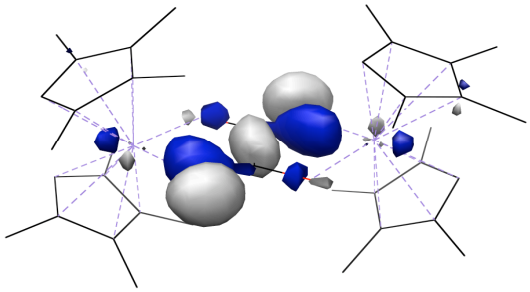
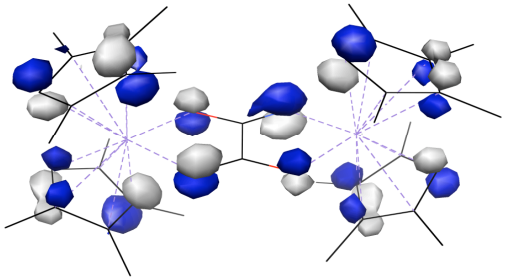



**Figure S5.** Representation of the solid state structure of (***R***)**-1-(I)(NCO)** at 30 % probability ellipsoids. Hydrogen atoms omitted for clarity.

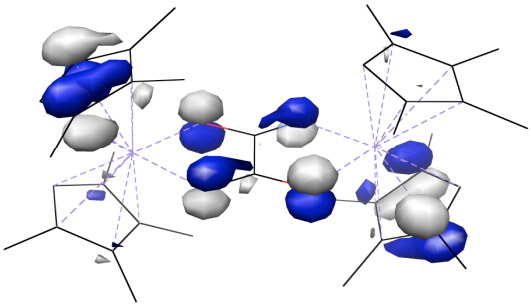
## IV. DFT-Computed Molecular Orbitals of 2.



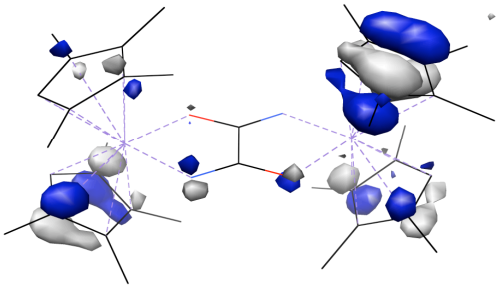
HOMO



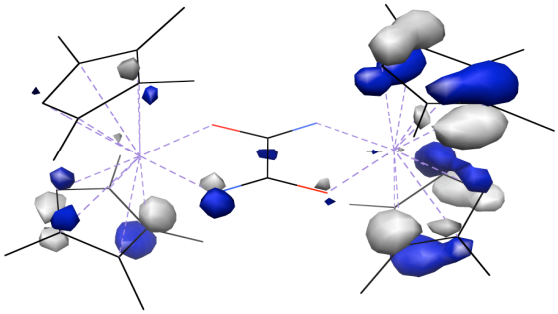
HOMO-1



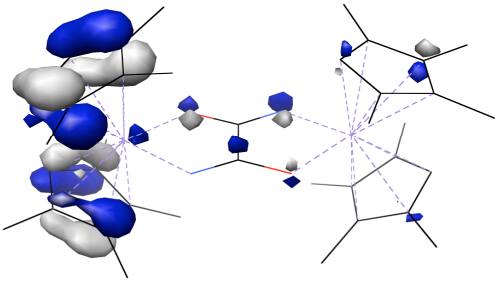
HOMO-2



HOMO-3



HOMO-4



HOMO-5

**Figure S6.** Highest occupied molecular orbitals of **2**.

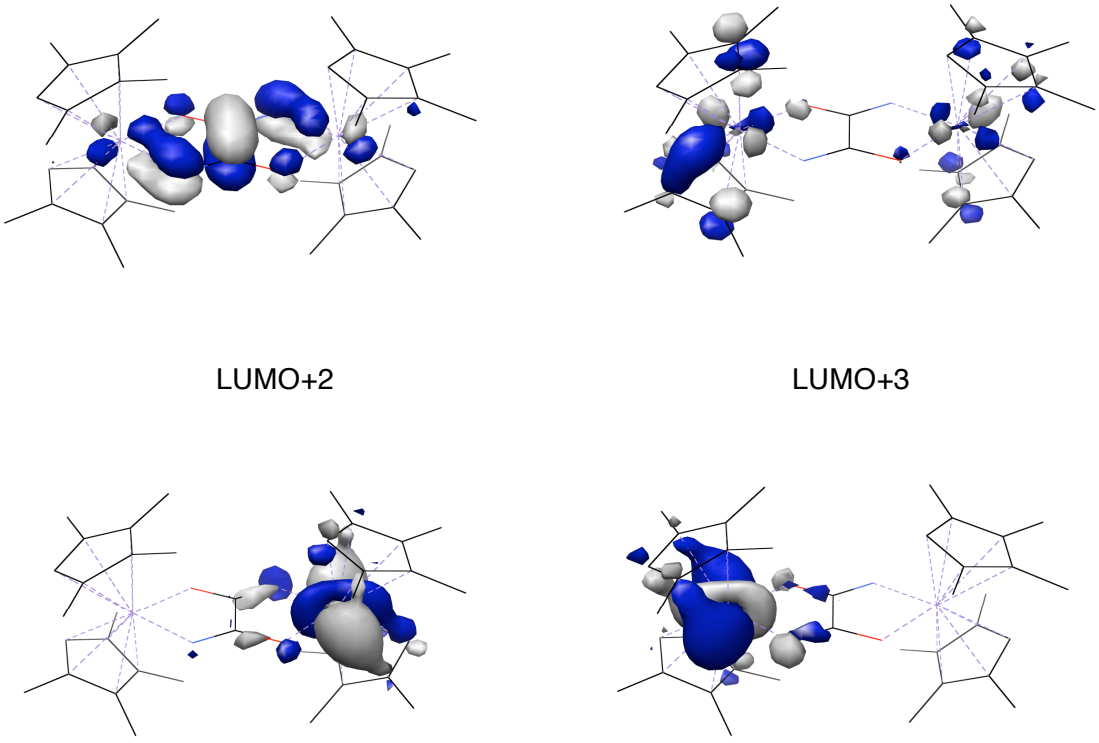



**Figure S7.** Lowest unoccupied molecular orbitals of **2**.

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